

# THE DETERMINATION OF CALCIUM

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## THE DETERMINATION OF CALCIUM

Calcium is usually the major cation in natural freshwaters, and is derived from calcareous soils and 'softer' rocks which are particularly abundant throughout the southern portions of the province of Ontario. The greatest concentrations are found in ground waters in the southern Grand River area, where gypsum ( $\text{CaSO}_4$ ) deposits may contribute 800 mg/l or more of calcium. Normally less than 200 mg/l is found in ground waters, and less than 100 mg/l in surface waters. In hard rock areas (Precambrian Shield) there may be as little as 15 mg/l of calcium in surface waters, occasionally less.

The calcium content of lakes may be affected, especially if shallow, by the photosynthetic activity of aquatic plants and algae. In strong sunlight, this activity may absorb so much carbon dioxide that the pH is raised to levels at which calcium carbonate is precipitated, sometimes in such quantities as to form white marl beds on the lake bottom.

The solubility of calcium carbonate is governed by the concentration of calcium bicarbonate and carbon dioxide. Any mechanism which increases the concentration of carbon dioxide increases the solubility of the carbonate.

Calcium is an essential element for all life forms, enhancing biological productivity in plants, and is required for proper bone and teeth formation in humans and other animals. It is non-toxic and no limits have been proposed for its concentration in drinking or other waters. Calcium is usually the major component of hardness and is objectionable when it deposits out in hot water tanks, distribution systems etc. For this reason the hardness components (calcium and magnesium) are sometimes replaced by sodium using a water softener.

### 1. Sample Handling and Preservation

Glass or plastic containers are acceptable. Sample containers must be filled completely so that no air bubble remains after the containers are sealed. This preservation system should not be attempted during very cold weather because of the danger of freezing and possible breakage of samples in transit. This precaution will prevent the loss of dissolved carbon dioxide and prevent the precipitation of calcium as calcium carbonate. Natural surface water samples do not normally contain enough calcium, but ground water samples from wells and springs may contain enough dissolved mineral salts that precipitation is a major concern. Immediate delivery to the laboratory is the best precaution when forwarding such unstable samples.

## 2. Selection of Method

Three methods are employed for the determination of calcium. Method A, a manual compleximetric titration with EDTA is used routinely for ground water supplies where higher levels of calcium are usually encountered. Surface waters may also be analyzed by this method providing the samples are not excessively turbid or heavily colored and do not contain interfering substances in significant amounts.

Method B, analysis by automated Atomic Absorption Spectrophotometry, is used routinely for surface water samples or where it is not feasible to employ the manual titration procedure. Analysis of industrial effluents and sewage samples are usually carried out by a manual atomic absorption procedure as described in the *Determination of Trace Metals*.

As stated in the *Determination of Hardness*, a total hardness can be calculated by multiplying the calcium concentration by 2.49 and the magnesium concentration by 4.12 to yield their equivalent calcium carbonate concentrations. The summation of these two values yields the hardness concentration (as  $\text{CaCO}_3$ ).

CALCIUM  
COMPLEXIMETRIC TITRIMETRIC METHOD A

SUMMARY

Substance determined.	Calcium ion, $Ca^{++}$ .
Interpretation of results.	Results are reported as $mg/l$ $Ca$ .
Principle of method.	An aliquot of sample, buffered to a high pH, is manually titrated with standard $0.01$ M EDTA, to an endpoint indicated by ammonium purpurate.
Time required for analysis.	Approximately <i>5 minutes</i> are required for a single analysis. On a routine basis about <i>80</i> tests can be performed in a day.
Range of application.	$2 - 200$ $mg/l$ $Ca$ . Higher levels are determined by dilution.
Standard deviation.	$\pm 1$ $mg/l$ in the range $2 - 200$ $mg/l$ .
Accuracy.	Within the precision of the method.
Limit of detection.	$2$ $mg/l$ .
Interferences and shortcomings.	Acidic samples from industrial sources will require additional amounts of sodium hydroxide. Some metal ions may cause fading or indistinct endpoints. Copper in concentrations greater than $2$ $mg/l$ will titrate as calcium. Orthophosphate will precipitate calcium at the pH of the test if present in concentrations greater than $10$ ppm. Alkalinity in excess of $30$ $mg/l$ may cause indistinct endpoints with hard water samples.  THE TITRATION SHOULD BE PERFORMED IMMEDIATELY AFTER ADDITION OF THE INDICATOR BECAUSE IT IS UNSTABLE UNDER ALKALINE CONDITIONS.

## SUMMARY

Minimum volume of sample. 125 ml.

Preservation and sample container. Polyethylene or glass containers are suitable. With samples containing large amounts of carbon dioxide the glass containers must be filled to capacity and tightly sealed to prevent loss of carbon dioxide gas. Sample should not be allowed to freeze otherwise breakage will occur.

Safety considerations. Normal laboratory safety procedures should be followed.

CALCIUM  
COMPLEXIMETRIC TITRATION METHOD A

1. Introduction

A portion of sample is pipetted into a white porcelain casserole and buffered to a pH between 12 and 13, which precipitates most of the magnesium. The sample is then titrated with 0.01 M ethylenediamine tetraacetic acid (EDTA). At this pH ammonium purpurate (Murexide), used as an end-point indicator changes from pink to purple, the point at which all of the ionic calcium has been converted to an EDTA complex.

2.. Interferences and Shortcomings

Samples from industrial sources with pH significantly less than 7.0 may require a large addition of sodium hydroxide to produce the proper pH for analysis.

Orthophosphate, if present in concentrations greater than 10 mg/l P will precipitate calcium at the pH of the test and cause low results.

The following concentrations of ions cause no interference under conditions of the test:

Copper	2 mg/l Cu
Iron	20 mg/l Fe
Manganese	10 mg/l Mn
Zinc	5 mg/l Zn
Lead	5 mg/l Pb
Aluminum	5 mg/l Al
Tin	5 mg/l Sn

Alkalinity in excess of 30 mg/l  $\text{CaCO}_3$  may cause an indistinct endpoint with hard waters.



3. Apparatus

- a) Burette, 25 ml, auto-zero pressure fill type
- b) Magnetic stirrer and 1 inch spinbars (5)
- c) 250 ml, flat bottom, white porcelain casseroles (20)
- d) Oxford auto pipettor
- e) Volumetric pipets, 5, 10, 25, 50, 100.
- f) Volumetric flask, 1 liter
- g) Reagent bottle, 1 liter, clear, with ground glass stopper.

#### 4. Reagents

- a) Ethylenediamine tetraacetic acid, disodium salt, reagent grade, powder.
- b) Ammonium purpurate (Murexide) indicator, tablets.
- c) Anhydrous calcium carbonate, reagent grade, powder.
- d) Sodium hydroxide, reagent grade, pellets.
- e) Standard Calcium Carbonate Solution (1.00 mg  $\text{CaCO}_3$  per 1.00 mL)

Weight 1.000 g anhydrous calcium carbonate into a 500 mL Erlenmeyer flask. Slowly add 1:1 V/V HCl until all the  $\text{CaCO}_3$  has dissolved. Add 200 mL distilled water and boil for a few minutes to expel  $\text{CO}_2$ . Cool, add a few drops of methyl red indicator and adjust to the intermediate orange color by adding 3N  $\text{NH}_4\text{OH}$  or 1:1 (v/v) HCl as required. Transfer to a 1 liter volumetric flask, fill to the mark with de-ionized distilled water and mix. Store the solution in a glass reagent bottle.

- f) Standard EDTA Titrant 0.01 M (equivalent to 1.00 mg  $\text{CaCO}_3$  per 1.00 mL)

Dissolve 74.46 g disodium ethylenediamine tetraacetic acid dihydrate in 20.0 liters of deionized distilled water. Standardize (see *Determination of Hardness*).

- g) Sodium Hydroxide Solution, 1N

Dissolve 40 g sodium hydroxide in 1 liter of de-ionized distilled water.

#### 5. Procedure

- a) Select a sample aliquot volume, usually 50 mL, which will require a titrant volume ranging from a low of 3 to a maximum of 15 mL. The lower titrant volume limit restricts loss of precision due to the measurement of small volumes. A trial titration may be necessary to gauge the proper sample volume. Use a 100 mL aliquot if the titration requires less than 3 mL of titrant.
- b) Pipet this aliquot of sample into a casserole containing a spin bar.

- c) Add sufficient sodium hydroxide, normally 2 ml to raise the pH of the sample to between 12 and 13. Samples having a low pH (i.e. below 4.0) may require additional base to bring them to a pH between 12 and 13. Use a pH meter to ascertain the base requirement.
- d) Add 1 tablet of ammonium purpurate (Murexide) indicator, crushing the tablet if necessary with a clean glass rod, which should then be rinsed into the casserole.
- e) Place the casserole on a magnetic stirrer and commence titration with standard 0.01 M EDTA.
- f) With continuous stirring, titrate the sample to the ammonium purpurate (Murexide) endpoint (pink to purple).

THE TITRATION SHOULD BE PERFORMED IMMEDIATELY AFTER  
ADDITION OF THE INDICATOR BECAUSE IT BREAKS DOWN  
UNDER ALKALINE CONDITIONS

## 6. Calculation and Reporting

Results are calculated as mg/l Ca:

$$\text{mg/l Ca} = \frac{A \times B \times 400.8}{\text{ml sample}}$$

Where A = ml titration for sample

B = mg CaCO<sub>3</sub> equivalent to 1.00 ml EDTA

Results are reported in mg/l as Ca, according to the following schedule:

<u>Range in mg/l</u>	<u>Report in mg/l</u>
1 - 9	1 significant figure
10 - 99	2 significant figures
100 - 999	3 significant figures

## 7. Precision and Accuracy

The standard deviation is  $\pm 1$  mg/l based on a large number of samples analyzed in duplicate and is independent of concentration in the range 2 - 200 mg/l.

8. Bibliography

- i) Standard Methods for the Examination of Water and Wastewater, APHA, 13th ed., 1971.*
- ii) Study and Interpretation of the Chemical Characteristics of Water, Geological Survey Water Supply Paper No. 1473, U.S. Dept. of Interior.*

CALCIUM

ATOMIC ABSORPTION SPECTROPHOTOMETRY METHOD B

SUMMARY

Substance determined.	Calcium as $Ca^{++}$ .
Interpretation of results.	Results are reported as $mg/l$ Ca.
Principle of method.	An automated atomic absorption method is used to measure the concentration of calcium ions. The sample is diluted with a releasing agent, lanthanum chloride, prior to aspiration into the burner flame.
Time required for analysis.	About 200 samples may be analyzed in one day.
Range of application.	Working ranges are: 0 - 20 $mg/l$ Ca 0 - 100 $mg/l$ Ca
Standard deviation.	$\pm 0.26$ for the range 0 - 20 $mg/l$ Ca $\pm 1.3$ for the range 0 - 100 $mg/l$ Ca
Accuracy.	Within the precision of the method.
Limit of detection.	0.86 $mg/l$ Ca.
Interferences and shortcomings.	Alkali metals such as sodium, potassium, lithium and magnesium tend to cause an enhancement in absorbance, while other interferences such as aluminum, phosphate, silicate and sulfate tend to depress the calcium absorbance.
Minimum volume of sample.	50 $mL$

## SUMMARY

### Preservation and sample containers.

Glass or plastic bottles are acceptable. With samples containing large amounts of carbon dioxide, the sample containers must be filled to capacity and tightly sealed to prevent loss of  $CO_2$  gas. Sample should not be allowed to freeze otherwise breakage will occur.

### Safety considerations.

The possibility of burner flash-back or explosion is always present when using flame atomic absorption apparatus. The manufacturer's instructions for burner ignition, use, and shut-down should always be rigorously followed, and the waste trap filled with water at all times. Standard safety procedures should be employed when working with compressed gas cylinders. Caution should be exercised during the preparation of the lanthanum chloride since concentrated acid is used.

## CALCIUM

### ATOMIC ABSORPTION SPECTROPHOTOMETRY METHOD B

#### 1. Introduction

The sample under test, automatically mixed with a releasing agent, lanthanum chloride, is aspirated as a fine mist into the air-acetylene flame of an atomic absorption spectrophotometer. Light emitted from a hollow cathode lamp at a characteristic wavelength for calcium, is directed through the flame into a monochromator and onto a detector. Calcium atoms, heated in the flame absorb this light and the detector measures the decreased intensity of the resulting beam. The amount of light absorbed is directly proportional to the concentration of calcium in the sample, and is recorded on a strip-chart recorder as a series of peaks, then compared to a calibration curve derived from simultaneously tested standards. The calibration curve is linear throughout the working range.

#### 2. Interferences and Shortcomings

In an air-acetylene flame, alkali type metals such as sodium, potassium, lithium and magnesium if present in significant quantities, cause an enhancement in calcium absorbance. Other interferents such as *Al, Be, Cr, Fe, Ti, Zn, F, SO<sub>4</sub>, SiO<sub>2</sub>, PO<sub>4</sub>*, if present in significant amounts will depress the calcium absorbance. A releasing agent such as lanthanum chloride is used to overcome the depressing effects of these interferences.

Partial clogging of the burner nebulizer and consequent reduction in aspiration may result from processing samples containing large amounts of suspended solids; pre-filtration of samples is advisable in this case.

#### 3. Apparatus

- a) Unicam SP 1900 Double Beam Atomic Absorption Spectrophotometer, placed under an exhaust canopy.
- b) Corning double pen recorder, Model #845 or equivalent.
- c) Gilson Sample changer, Model #TD1 St/SC1 5 with 200 sample positions.
- d) Gilson Minipulse II pump, Model #HP 8.
- e) Manifold as outlined in *Figure I* and *Figure II*.

- f) Test tubes, 17 mm X 150 mm (400).
- g) Test tube racks for above tubes (8).
- h) Air and acetylene, suitable for atomic absorption analyses.
- i) Stabiline Automatic Voltage Regulator, Type IES9101B, Superior Electric Co.

THE BURNER HEAD SHOULD BE CLEANED FREQUENTLY WITH  
DETERGENT AND RINSED THOROUGHLY WITH DISTILLED WATER.



#### 4. Reagents

- a) Lanthanum oxide,  $\text{La}_2\text{O}_3$ , reagent grade powder.
- b) Hydrochloric acid,  $\text{HCl}$ , concentrated, Aristar grade.
- c) Calcium carbonate,  $\text{CaCO}_3$ , reagent grade powder.
- d) Combined Stock Standard Solution

For the determination of sodium, potassium, calcium and magnesium by atomic absorption spectrophotometry, a combined stock standard solution is prepared with the following concentrations:

Calcium	2000 mg/l
Magnesium	600 mg/l
Sodium	1000 mg/l
Potassium	600 mg/l

Refer to the individual method write-ups for the preparation of each stock solution.

#### e) Stock Standard Calcium Solution

Place 9.9888 g of reagent grade calcium carbonate (dried) into a clean 500 mL Erlenmeyer flask and carefully add 50 mL of 1:1 v/v hydrochloric acid in small quantities, swirling the flask periodically. When dissolution is complete, transfer the contents of the Erlenmeyer flask to a 2000 mL volumetric flask, rinse the Erlenmeyer flask several times with deionized distilled water, each time adding the rinses to the volumetric flask. Add each of the stock standard portions prepared for sodium, potassium and magnesium to the contents of this 2000 mL volumetric flask and dilute to the mark with deionized distilled water. Thoroughly mix the solution and transfer to a plastic reagent bottle.

#### f) Working Standard Solutions

Daily calibration standards are prepared for each range as required by diluting the following aliquots to 1000 mL.

High Range

Combined Stock Standard Solution ml	50.0	40.0	30.0	20.0	10.0	5.0
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Working Standards mg/l Ca	100	80	60	40	20	10
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Prepare an intermediate standard solution by diluting 200 ml of Combined Stock Standard Solution to 1000 ml (400 mg/l Ca).

Low Range

Intermediate Standards Solution ml	50.0	40.0	30.0	20.0	10.0	5.0
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Working Standards mg/l Ca	20	16	12	8	4	2
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g) Lanthanum Chloride Solution

Dissolve 16.00 g  $\text{La}_2\text{O}_3$  in 200 ml deionized distilled water containing 30 ml concentrated hydrochloric acid. When the salt is completely dissolved, dilute to 4000 ml with deionized distilled water and mix thoroughly. The pH of this solution should be approximately 1.7. Store solution in plastic bottle.

i) High Range Calcium (0 - 100 mg/l)

For this range, 4.00 ml of  $\text{LaCl}_3$  solution is proportioned with sample using the manifold shown in Figure II. This yields a lanthanum concentration of approximately 3090 mg/l at the burner head.

ii) Low Range Calcium (0 - 20 mg/l)

For this range, 2.42 ml of  $\text{LaCl}_3$  solution is proportioned with the sample using the manifold shown in Figure I. This yields a lanthanum concentration of approximately 1870 mg/l at the burner head.

h) Quality Control Samples

Prepare Quality Control A and B Solutions, QC-A and QC-B respectively, that will provide test solution for at least 20 DAYS of analysis. The concentration of the QC-A and QC-B should be chosen such that they fall within the normal concentration range of samples being routinely analyzed. These quality control checks are used to detect systematic error such as blank or calibration changes from day to day and must be included in each run of standards and samples on a day to day basis. When preparing new QC-A and QC-B solutions, do so EARLY and monitor their response in comparison with the old set for at least THREE DAYS prior to adopting them.

5. Procedure

- a) List the samples which require analysis on a bench sheet designed for 10 samples each. Use separate bench sheets for different sample classifications.
- b) Collect the necessary samples maintaining the same sample sequence as listed on the bench sheets.

*MAINTENANCE OF SEQUENTIAL SAMPLE ORDER IN COLLECTION AND RETURN OF SAMPLES TO THEIR PROPER STORAGE POSITION, AND IN LISTING, PREPARATION AND ANALYSIS, GREATLY ASSISTS IN ENSURING THAT BENCH SHEETS AND SAMPLES ARE PROPERLY CORRELATED AND ALSO FACILITATES THE REPORTING OF RESULTS AND AN ORDERLY LABORATORY WORK RECORD.*

- c) Using a well mixed sample, rinse a test tube a minimum of three times with sample prior to introducing an aliquot for analysis.

*SAMPLES FOR ANALYSIS MUST BE AT ROOM TEMPERATURE IN ORDER TO AVOID POSSIBLE SENSITIVITY CHANGES.*

- d) Place the test tube containing the sample into a test tube rack in such a position that it may easily be correlated with the sample number on the bench sheet i.e. the 4th sample on the 2nd sheet is located in the 4th space in the 2nd row of the test tube rack. Where empty spaces occur on the bench sheet, leave the corresponding space in the test tube rack vacant. Write the appropriate sample number on the first and last sample tube in each row.

- e) Set the atomic absorption spectrophotometer into operation as outlined under Operational Steps.
- f) When loading the samples into the Gilson sampler module, ensure that bench sheets are retained in the proper order by clipping them in sequence, one at a time, on a clip board as each row of samples is loaded.
- g) Complete Sampler Loading Sequences.

Each run of samples will include all of the following units:

Set of standards		Stds
Distilled water blank		Bl
Quality control samples	A:	A
	B:	B
Sensitivity monitoring standards	High	H
	Low	L
Samples in groups of 10 or less:		<u>10</u>

The sample loading sequence is as follows:

H; Bl; H; Bl; H; Bl; 6 Stds; Bl; QC-A; QC-B; Bl;  
n (10; Bl); (10, L, H, Bl)

where n is the number of repetitive units of samples.

- h) Commence the run at any time there is sufficient work to allow uninterrupted operation of the Atomic Absorption Unit.

THE AAS UNIT MUST NOT BE LEFT UNATTENDED WHILE IT IS IN OPERATION.

- i) Determine if the standards and quality control checks agree with previous results.
- j) Mark off each group of peaks on the chart paper which correspond to a single bench sheet. Assign a sequential page number to each group of 10 or less sample peaks and assign the same number to the associated bench sheet.

- k) Record the measured values of the QC-A and QC-B as well as the values of the Highs and Lows.
- l) The peak heights obtained for the samples are converted directly to concentration units by comparison to known standards using either a calibration curve or digitizing system.

Operational Steps:

The Unicam SP 1900 Atomic Absorption Spectrophotometer is a double beam ratio measuring instrument with digital display. Calcium analyses are performed on the absorbance mode utilizing an air-acetylene flame. The following is a general guide to the operation of this unit. More detailed information regarding the instrument is available in the 'Users Manual'.

- 1) Turn on the instrument in the following sequence:

- i) voltage stabilizer
- ii) main power switch
- iii) readout section - Corning double pen recorder
- iv) appropriate hollow cathode lamp current

ALLOW A MINIMUM OF 15 MINUTES WARM UP.  
ENSURE THAT THERE IS SUFFICIENT WATER  
IN THE WASTE TRAP.

- 2) Set the following controls to their predetermined optimum values; for calcium:
  - a) lamp current = approximately 50% of rated lamp current
  - b) slit width = 0.20 mm
  - c) wavelength = 422.7 nm
  - d) burner height = 0.5 cm

- 3) Set the digital display selector switch to the set-up mode and adjust the sensitivity control knob so that the energy pointer is approximately mid point in the blue sector of the ENERGY indicator. Observe the ENERGY meter or the digital display and re-adjust the WAVELENGTH control moving it slightly to either side of the nominal setting until the maximum energy is obtained (maximum deflection to the right on the ENERGY meter scale or largest negative value on the digital display). If the energy pointer does not remain in the blue sector, adjust the sensitivity control knob and/or the lamp current output.

*THE OPTIMUM SET-UP VALUE OF THE DIGITAL DISPLAY AND SENSITIVITY IS TO BE NOTED AND MAINTAINED DAILY.*

- 4) Set the selector switch to the absorption mode. The energy pointer should remain in the blue sector.

*IF THIS IS NOT THE CASE IT IS AN INDICATION THAT CERTAIN PARAMETERS (LAMP CURRENT, WAVELENGTH, SLIT WIDTH OR LAMP ALIGNMENT ETC.) MAY HAVE BEEN INCORRECTLY SET. THEY SHOULD BE CHECKED IN SEQUENCE AS NECESSARY.*

- 5) Turn on the air pressure (support) and adjust to the recommended value, (5.0 L/min).
- 6) Turn on the acetylene (fuel) to the recommended value, (900 cc/min).
- 7) Set the FUEL ON/OFF control to the UP (ON) position. When the acetylene and air have been flowing for about 5 seconds, depress and hold the IGNITION switch, releasing it when ignition occurs at the burner head.
- 8) Aspirate the suppressant, lanthanum chloride into the flame, depress the ZERO button and adjust the baseline on the recorder.

9) Optimizing the Signal Output

For the working range selected, aspirate the high standard into the flame and note the absorbance reading and peak height. The absorbance should read approximately 0.500 absorbance units and the peak height should be 90% of full scale. If these conditions cannot be achieved, then carefully adjust the impact head to achieve the desired result. If the system is oversensitive, re-adjust the impact head and/or rotate the burner head accordingly. Once they are achieved, optimum conditions should be recorded. They should not change drastically from day to day.

LOCK BURNER CHAMBER DOOR.

10) Proceed with analyses.

11) Shut down the instrument in the following sequence:

- i) Turn off FUEL supply
- ii) Turn off Air supply
- iii) Shut off recorder
- iv) Shut off lamp current control
- v) Shut off main power switch on AAS unit.
- vi) Shut off voltage stabilizer

THE DANGER OF BURNER FLASH-BACK AND/OR EXPLOSION IS ALWAYS PRESENT WHILE USING FLAME ATOMIC ABSORPTION APPARATUS. THE MANUFACTURER'S PROCEDURES SHOULD BE CAREFULLY FOLLOWED FOR IGNITION, USE AND SHUT-DOWN OF THE BURNER. NORMAL SAFETY PRECAUTIONS MUST ALWAYS BE EXERCISED WHEN TRANSPORTING AND USING COMPRESSED GAS CYLINDERS.

6. Calculation and Reporting

The peak heights are converted directly to concentration units,  $\text{mg/l Ca}$ , by a calibration curve or the Hewlett Packard digitizer. Results are reported as follows:

<u>Range</u>	<u>Report to</u>
0 - 20 $\text{mg/l}$	3 significant figures
0 - 100 $\text{mg/l}$	2 significant figures

7. Precision and Accuracy

<u>Standard Deviation</u>	<u>Duplicates</u>	<u>Range (mg/l)</u>
$\pm 0.26 \text{ mg/l Ca}$	Within-run	0 - 20 $\text{mg/l}$
$\pm 1.3 \text{ mg/l Ca}$	Within-run	0 - 100 $\text{mg/l}$



8. Bibliography

- i) *Standard Methods for the Examination of Water and Wastewater*, 13th ed., APHA Washington D.C.; 1971
- ii) *Users Manual, Unicam SP1900 Series Atomic Absorption Spectrophotometers*. Pye Unicam Ltd., Cambridge, England, Publication No. 299408.
- iii) *Outlines of Analytical Methods*, Ontario Ministry of the Environment, Laboratory Services Branch, February 25, 1975.

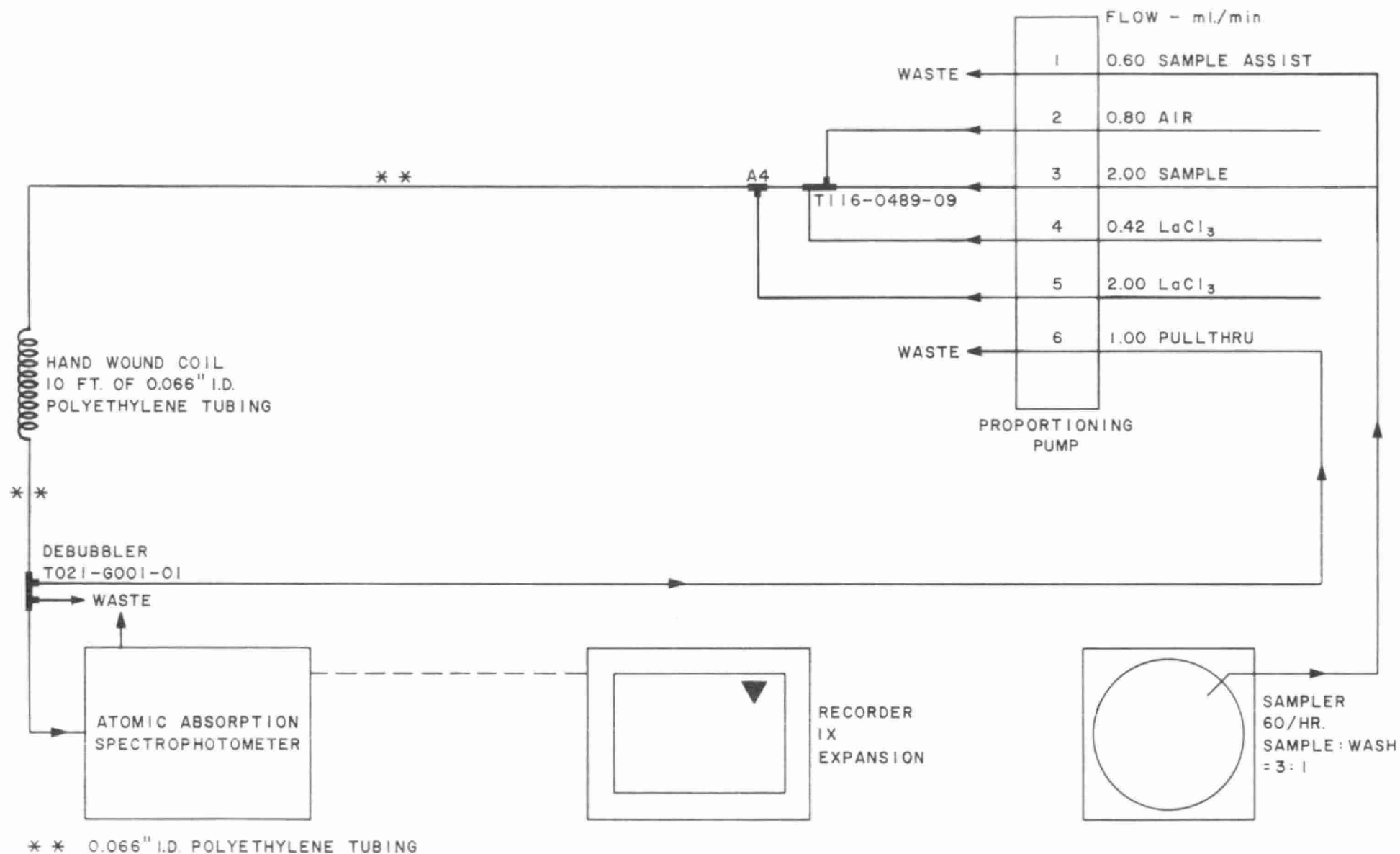


FIGURE I - ATOMIC ABSORPTION MANIFOLD FOR CALCIUM - METHOD 'B'  
RANGE: 0-20 mg/l

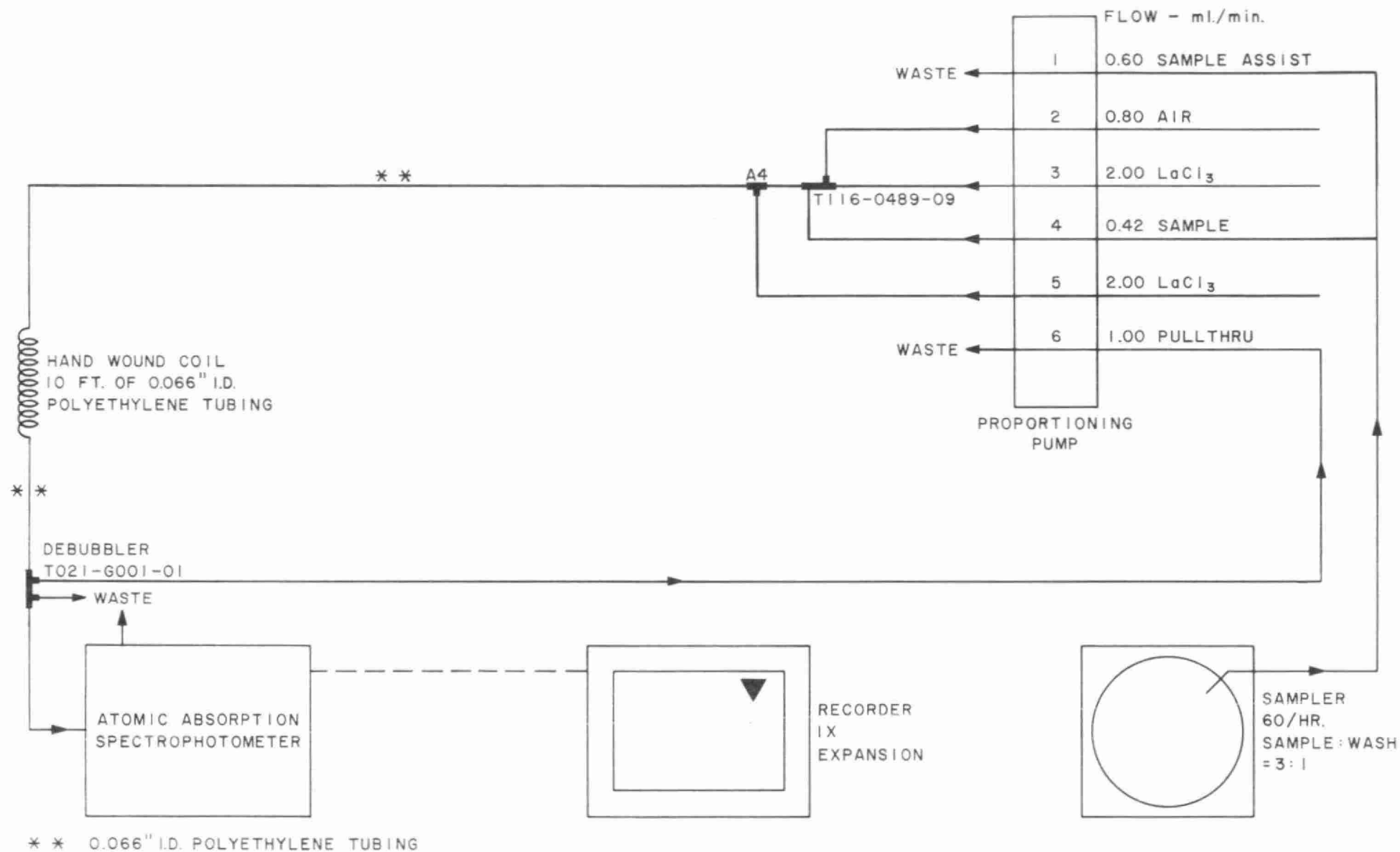


FIGURE II - ATOMIC ABSORPTION MANIFOLD FOR CALCIUM - METHOD 'B'  
RANGE: 0-100 mg/l

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